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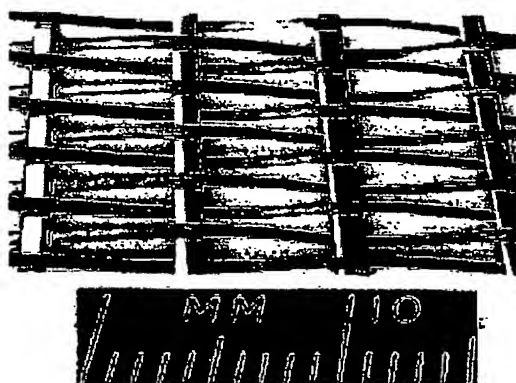
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(54) Title: **MEDICAL FIBRES & FABRICS**



(57) Abstract: A fibre or fabric comprising silicon for use as a medical fibre or fabric. The silicon present can be biocompatible, bioactive or resorbable material and may also be able to act as an electrical conductor. In addition, porous silicon may be used as a slow release means for example for drugs or fragrances, or as a collector for example for sweat. Novel fibres, fabrics and methods of preparation of these are also described and claimed.

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## MEDICAL FIBRES &amp; FABRICS

The present invention relates to fibres and fabrics containing silicon for use as medical fibres and fabrics, as well as to novel fibres and fabrics suitable for these applications and others, and to methods for their production.

The production of fibres and fabrics is an ancient art. Fibres suitable for textile use possess adequate length, fineness, strength and flexibility for yarn formation and fabric construction. The first fibres available for textile use were obtained from animal and plant sources. Cotton, wool, jute, silk and flax are today the most common natural fibres. Nylon, rayon and polyester are common synthetic fibres.

It is now possible to manipulate ultrafine fibres into fabrics, for example using techniques used to produce woven metallic jewellery and Denier-grade stockings. Nylon fibres created by spinnerets for example have diameters of about 25 microns.

The use of fabrics and other fibrous forms as biomaterials dates back to the early Egyptians and Indians. Linen strips and sutures were used with natural adhesives by the Egyptians to draw the edges of wounds together. The American Indians used horsehair, cotton and thin leather strips for similar purposes. Use of fabrics as biomaterials was initially viewed as a new application of conventionally woven and knitted textiles. Over the past few decades the development of sophisticated polymer and fibre processing technologies, nontraditional fabric forms and fibrous products have also been employed.

These products may have a variety of medical applications, depending upon their precise nature and form. For example, fibres and fabrics may have general surgical applications, for examples as sutures, threads or meshes. In the cardiovascular fields, they may be incorporated for example in artificial heart valves. Orthopaedic prostheses such as tendons and

ligaments utilise products in the form of fibres and fabrics and they may also have percutaneous/cutaneous applications such as in shunts and artificial skin.

- 5 The particular materials currently used in medical textiles include modified natural polymers, synthetic nonabsorbable polymers and synthetic absorbable polymers.

However, most commercial polymer textile fibres have various  
10 additives (such as dyes, antistatic agents, delustrants, photostabilisers) which may reduce their biocompatibility and thus limit the options for using these in medical applications. Although some may be biodegradable, it is difficult to ensure that fibres do not lose their mechanical strength at too early  
15 a stage in the tissue replacement process.

The applicants have developed new medical fibres and textiles.

According to the present invention there is provided a fibre or  
20 fabric comprising silicon for use as a medical fibre or fabric.

As used herein, the term "silicon" refers to elemental silicon material which is a semiconductor. For the avoidance of doubt, it does not include silicon-containing chemical compounds such  
25 as silica, silicates or silicones, although it may include composites of semiconducting silicon combined with medical-grade polymer, ceramic or metal phases. It may also include doped semiconducting silicon where concentrations up to the atomic percent level of elements like boron or phosphorus are  
30 incorporated into the silicon lattice to raise electrical conductivity. Porous silicon may be referred to as "pSi", crystalline silicon as "c-Si" and amorphous silicon as "a-Si".

Silicon has several particular advantages for use in this way.  
35 In particular, fibres and fabrics can be produced with a wide range of desirable properties, including biocompatibility, resorbability or biodegradability or bioactive properties.

Furthermore, such fibres or fabrics may have semiconducting properties, which may be particularly useful in the context of certain applications, for example, in implants, prostheses and the like, where controlled levels of electric current may be applied to stimulate incorporation into the body.

As used herein, the term "fibre" refers to a unit of matter having length at least 100 times their diameter or width.

- 10 The term "fabric" may be defined as thin, flexible and porous materials made by any combination of cloth, fibre or polymer. Cloth is a thin flexible material made from yarn, and yarn comprises a continuous strand of fibres.
- 15 The expression "bioactive" refers to materials, which when used in vivo, elicit a specific biological response that results in the formation of a bond between living tissue and that material.
- 20 "Biocompatible" as used herein refers to materials which, in thin film form, are acceptable for use in at least some biological applications.

As used herein, the term "resorbable" relates to material which will dissolve at normal physiological temperatures ( $37^{\circ}\text{C} \pm 1^{\circ}\text{C}$ ) in simulated body fluid, over a period of time, for example of up to 8 weeks, and generally at less than 2 weeks. Simulated body fluid in this case may comprises a solution of reagent grade salts in deionised water so that the ionic concentration reflect that found in human plasma, as shown in the following Table 1, or alternatively it may comprise a simulated synovial fluid, sweat, urine, or other body fluids. In simulated human plasma, the mixture is buffered to physiological pH values ( $7.3 \pm 0.05$ ), preferably organically, using for example trihydroxymethylaminomethane and hydrochloric acid.

Table 1

Ion	Concentration (mM)	
	Simulated Body Fluid	Human Plasma
$\text{Na}^+$	142.0	142.0
$\text{K}^+$	5.0	5.0
$\text{Mg}^{2+}$	1.5	1.5
$\text{Ca}^{2+}$	2.5	2.5
$\text{HCO}_3^-$	4.2	27.0
$\text{HPO}_4^{2-}$	1.0	1.0
$\text{Cr}^-$	147.8	103.0
$\text{SO}_4^{2-}$	0.5	0.5

WO 97/06101 describes the formation of silicon in a form in which is it biocompatible, bioactive and/or resorbable.

In a particularly preferred embodiment, the silicon used in the invention is porous silicon. Porous silicon may be classified depending upon the nature of the porosity. Microporous silicon contains pores having a diameter less than 20Å, mesoporous silicon contains pores having a diameter in the range of 20Å to 500Å; and macroporous silicon contains pores having a diameter greater than 500Å. The nature of the porosity of the microparticles or fibres of silicon used in the invention may vary depending upon the intended use. Factors such as the need for biocompatibility, resorbability and bioactivity need to be balanced against the need for mechanical strength and other physical factors discussed more fully below.

In particular the silicon used in fibres and fabrics for use as medical fibres and fabrics is mesoporous silicon, which is resorbable.

The silicon fibre or fabric which is the subject of the invention may take various forms, some of which are novel and these form further aspects of the invention.

In one embodiment, silicon containing fibres for use in the invention are prepared by incorporating silicon microparticles, and preferably porous silicon microparticles, to a preformed fabric. This may comprise any of the known fabrics, but in particular is a biocompatible fabric such as cotton, linen or a biocompatible synthetic fabric.

Preferably the silicon microparticles are bound to the surface of the fabric by covalent bonds. This can be achieved in various ways. For example, hydroxy groups may be formed on the surface of the silicon, for example by treatment with ozone in the presence of U.V. light. These may then be reacted with surface groups on the fabric directly, or more preferably, they may first be functionalised with a reactive group. Examples of such functionalisation reactions are described in WO 00/66190 and WO 00/26019.

In particular the microparticles are bound by reaction with a compound of formula (I)



where Y is a leaving group such as trimethoxysilane, R is a linking group, such as C<sub>1-6</sub>alkylene and in particular C<sub>2-4</sub>alkylene such as propylene, and X is a reactive functionality, such as halo and in particular chloro. The reaction is suitably effected by appropriate input of thermal energy or light.

This reaction converts the surface hydroxy groups to groups of formula -O-R-X, where X and R are as defined above. Subsequent reaction with for example surface hydroxy groups on the fabric, will result in the silicon microparticle becoming covalently bound to the surface by an alkylether link. The subsequent reaction is suitably effected in an organic solvent such as toluene or an alcohol such as C<sub>1-4</sub>alkyl alcohols, at elevated temperatures, for example at the reflux temperature of the solvent.

Thus a further aspect of the invention comprises a fabric having silicon microparticles incorporated therein. In particular, the silicon microparticles are covalently bound to the fabric.

5

The inclusion of silicon microparticles, and particularly porous microparticles, will enhance the bioactivity of the fabric. Furthermore, silicon particles may be added at a sufficient density to bring about particle-to-particle contact which is able to provide an electrically continuous pathway. In this way, the fabric may acquire semi-conducting properties which may be of use in the medical application to which it is put.

10

15 Suitable fabrics include biomedical fabrics such as cotton, linen or synthetic polymers, which may be absorbable or non-absorbable.

In an alternative embodiment, silicon is incorporated into a fibre, which may then be processed into fabrics, either alone or in combination with other types of fibre.

20

The silicon fibres used may comprise silicon alone, or they may be in the form of a composite of silicon with other materials.

25

The preparation of some silicon and silicon composite fibres is known. For example, Japanese patent no. JP9296366A2 describes the preparation of composite fibres, fabricated by either vapour deposition of thin Si/SiO<sub>x</sub> films onto polyester fibres or spinning of a polyester/silicon mixture.

30

Pure Silicon fibres of varying crystalline perfection have also been realised by a number of techniques :

35 Single crystal silicon fibres and their preparation are described for example by B.M.Epelbaum et al. in Cryst. Res. Technol. 31, p1077-1084 (1996). In this method a crucible containing molten Si is connected to a graphite nozzle that

acts as the shape defining die. Due to molten silicon having a low viscosity, high surface tension and high chemical reactivity, pulling of single crystal fibres is difficult. Three types of crucible die arrangement were designed and  
5 tested. Single crystal fibres of diameter in the range 100-150 microns and lengths up to 80mm were grown successfully. The maximum pulling speed achieved was 1mm/minute.

Laser-assisted chemical vapour deposition (LCVD) has been shown  
10 to provide a higher growth rate synthesis route for a wide variety of inorganic fibres, including silicon. In the LCVD technique a laser beam is focussed onto a point inside a reactor to initiate chemical vapour deposition in the direction of the laser. By moving the substrate at the same speed as the  
15 deposition rate, a continuous fibre is realised. For example, with the methods described by P.C.Nordine et al in Appl. Phys. A57, p97-100 (1993), silicon fibre growth rates up to 30mm/minute were achieved using silane gas pressure of 3.4 bar and Nd : YAG laser power up to 200mW. At fibre tip temperature  
20 of 525 - 1412 C, poly-Si fibres of 26-93 micron diameter were realised with varying degrees of crystallinity.

Silicon fibres have also been realised by the VLS method, as disclosed in the early paper of R.S.Wagner and W.C.Ellis in  
25 Appl. Phys. Lett. 4,p89-90 (1964). Here the V represents a vapour feed gas or gas mixture, the L represents a liquid catalyst and the S represents a solid fibre product. In this method it is the size of the metal catalyst droplets that primarily determine the resulting fibre diameter. The  
30 synthesis of both crystalline silicon microfibres and more recently, nanowires, has been demonstrated using, for example, gold as the catalyst and silane as the vapour phase reactant. There are also many related early reports of silicon  
35 "whiskers", "needles" and "filaments" of relatively short length (under 10 cms) as reviewed in Whisker Technology (John Wiley & Sons 1970), Edited by A.P.Levitt.

The VLS method should be adaptable to mass production of short



silicon fibres for air laying or wet laying. Incorporation of silicon onto/into pre-existing fibres / yarns should be most suitable for weaving, knitting and embroidery of structures of many metres length.

5

Silicon microwires and the preparation are described for example by J.J.Petrovic et al. J.Mater.Res. Oct Issue 2001. In this method, an optical FZ Si growth system was adapted to generate microwires by the "Taylor microwire technique". The material to be processed is melted within a glass tube and the softened glass with the molten material mechanically drawn out into a fine wire in a similar manner to that of drawing of optical glass fibres. The working temperature of the glass needs to exceed the 1410°C melting point of silicon, where the method was applied to pure silicon. In this study Vycor glass (Corning 7913) was used which has a softening temperature of 1530°C and a working temperature of 1900°C. A pure Si charge was loaded into evacuated tubes that were then heated to 1900°C using halogen lamps and mechanically pulled. Flexible 10-25 micron diameter poly-Si microwires were synthesised by this method in continuous lengths up to 46 cms.

J.F.Hetke et al. IEEE Trans.Biomed.Engn.41, 314-321 (1994) describes the design, fabrication and testing of "ultraflexible" ribbon cables for use with CNS microprobes. Standard Si wafers were subjected to photolithography, deep boron doping and multidielctric deposition to define the cables that were subsequently floated off by using a boron etch-stop and a fast wet etch to dissolve the underlying wafer. Cables as thin as 2-3 micron and as thick as 20 micron were realised by varying the boron diffusion temperature and time.

Multistrand cables containing 20-30 micron strands are also described here, and these provided "enhanced flexibility in the radial and lateral directions". An image of a 5 strand ribbon cable tied into a knot was shown to illustrate flexibility. Such designs had lengths of 1-5cms and total widths ranging

from 60-250 micron. Fibres produced in this way have good flexibility as illustrated in J.F.Hetke et al., Sensors and Actuators A21-23,999-1002 (1990), where a single 15 micron thick strand is shown bent through 180 degrees.

5

Although there are such examples of silicon fibres, fibre arrays of a form and structure suitable for medical fabric construction are novel, and as such form a further aspect of the invention.

10

The applicants have found that fibres may also be produced by cutting a silicon wafer using a saw with a sufficiently small blade and pitch, for example a 75-micron blade and a 225-micron pitch. Preferably, multiple parallel cuts are formed in a single wafer to form a comb like structure, which allows for the production of multiple fibres. In a particularly preferred embodiment, two such comb-like structures are produced, and then interweaved in a perpendicular manner. In this way, the fibres of one comb forms a waft and the fibres of the other wafer form a weft of a fabric like structure. Cut fibres may be subject to cleaning for example, ultrasonic cleaning, and/or etching, for example by anisotropic wet etch to remove saw damage and/or to shape the cross section of the fibres.

25 Other methods for producing silicon or silicon composite fibres may be used however. For example, hollow amorphous silicon microfibres may be obtained by coating a fibre, such as a polymer, metal, ceramic (including glass) fibre, preferably with a hollow core, with silicon and particularly amorphous or polysilicon. This may be achieved for example by sputtering or continuous vapour deposition (CVD). Subsequently the initial fibre can be dissolved, leaving a hollow amorphous or polysilicon microfibre. This may then be porosified if desired. If the initial fibre is a biocompatible material, for example a biodegradable suture, dissolution may not be necessary or desirable.

In an alternative embodiment, silicon fibres are formed by threading together silicon beads to form flexible chains on a resilient thread or wire, which is preferably a biocompatible or biodegradable suture. The resultant structure, which is  
5 novel and forms a further aspect of the invention, is therefore similar in structure to strings of beads found in jewellery. Individual silicon beads may be of various sizes, depending upon the intended nature of the fibre, or the fabric produced therefrom.

10

For example, beads may be on a macroscale, for example of from 0.5 to 5mm in diameter. In these cases, they may be formed by drilling holes through appropriately sized silicon granules and subsequently threading through the resilient thread or wire.

15

Where microscale beads are required, for example of from 10 microns-500microns diameter, they are suitably prepared by photolithography and surface micromachining. For example, a silicon membrane may be supported on a dissolvable surface,  
20 such as a silicon oxide surface. Trenches for example of up to 500 microns and preferably about 50 microns in depth can then be etched into the upper surface of the membrane for example by a dry etching or photolithographic process. A further silicon membrane may then be deposited over the surface, so that the  
25 trench forms a central cavity. This structure can then be etched photolithographically to the desired depth, representing the diameter of the desired bead, to form substantially parallel trenches on either side of the central cavity. Further channels may be etched which channels are substantially  
30 perpendicular to the trench to trace out the desired bead shape. Once this has been done, and a suitable thread or suture passed through the central cavity, the dissolvable surface may be removed.

35 These production methods form yet further aspects of the invention.

Fibres and composite fibres obtained using any of the above methods may be suitable for use in the invention. Preferably however, the fibres used are porous, or contain porous silicon beads and these can be obtained by porosifying the fibres or  
5 strings of beads produced as described above, using for example, methods described in US Patent No. 5,348,618 and Properties of Porous silicon (IEE 1997 Ed by L.T.Canham).

In a particular embodiment therefore, the invention provides a  
10 method of preparing a porous silicon fibre, which method comprises forming a silicon fibre, in particular by one of the melt pulling, Laser-assisted chemical vapour deposition (LCVD), VLS methods, coating of sacrificial fibrous material or micromachining methods described above, and thereafter  
15 porosifying the silicon, for example by anodisation or stain etching.

The applicants have found that porous silicon fibres may be produced directly by cleaving mesoporous films on silicon  
20 wafers. The films may be formed using conventional methods, for example by anodisation of a silicon wafer in hydrofluoric acid (HF) for example 40wt% HF, and ethanol, suitably in equal volumes. Fibres may be cleaved mechanically, for example by breaking them over a solid edge, for example of a glass  
25 surface, for instance a glass slide, which may be covered in filter paper. The wafer may be prescored or scribed before the breaking is carried out.

Porous or partially porous silicon containing fibres and  
30 fabrics are novel and as such form a further aspect of the invention.

Substantially pure silicon fibres, for example of length greater than 100cm, are also novel, and these also form an  
35 aspect of the invention. Preferably, these are porosified as discussed above.

As used herein the expression "substantially pure" means that the silicon is at least 98% pure, more suitably at least 99% pure, and preferably 100% pure.

5 For the purposes of the invention, fibres consisting of or comprising silicon can be used directly as sutures, if they have sufficient flexibility and strength. The factors required to achieve fibres having high levels of flexibility are discussed further below.

10

Alternatively, they may be converted into fabrics or yarns using one or more of any of the major processes common in textile manufacture. These include spinning, embroidery, weaving, knitting, braiding, fibre bonding, air-laying, wet  
15 laying, and laminating. The possibility of applying all these various techniques in the production of fabrics for medical use provides the opportunity to achieve complex 2-dimensional and 3-dimensional topographies. This may be particularly useful in certain applications, for example when the fabric is used to  
20 assist in-bone growth, open meshes would be preferred.

Silicon is a tough but brittle material and porous silicon is prone to cracking. It is hence surprising that porous fibres can be produced which are strong and flexible enough to be  
25 weaved into intricate patterns.

Most natural fibres such as wool, cotton and flax are not long enough to be processed into cloth without further treatment. They are converted to usable thread by a process known as  
30 spinning, where fibres are first laid out parallel to one another ("carded") and twisted together into a "yarn" (as illustrated for example in Figure 2 hereinafter). Such processes may also be applied to fibres comprising silicon.

35 Substantially pure silicon yarn is also novel, and forms yet a further aspect of the invention.

- Embroidery involves the formation of stitches on a base cloth, which means that there is a high flexibility in design. The base cloth may then be dissolved away after the stitching process is terminated. This process may be particularly good  
5 for mimicking natural fibrous arrays such as ligaments. There is also potential in fracture fixation where load bearing threads are arranged optimally with an open mesh for tissue in-growth.
- 10 The weaving process requires the interlacing of two separate sets of elements to produce a fabric. The element called "warp" is set down first, usually in a parallel arrangement; the second element called the "weft" then interlocks with the warp to create the stable planar structure. Weaving does not  
15 require too much fibre flexibility. In a simple mechanical loom, the warp threads run off a roller as wide as the finished bolt of cloth will be. The threads run through a set of wires running vertically which can be moved up and down. Each wire has a small eye or ring, in the middle through which the warp  
20 yarn runs. By simple mechanical arrangements it is possible to raise every alternate ring, making a space for which the weft can pass. The weft is carried by a "shuttle" or jets of air/water. When the weft has passed through the warp it is pushed down tightly against the previous thread with a comb-like frame. The rings carrying the warp threads are now  
25 depressed, the shuttle turned around and the second "pass" between a set of threads is made. The fastest industrial looms operate at around 200 passes a minute.
- 30 Woven fabrics usually display low elongation but high breaking strength. They may have a variety of 2D and 3D topography, depending upon the type of weave used, and typical examples are illustrated in Figure 1 herein after. If required, the 3D topography of a particular fabric can be modified by for  
35 example localised melting of the fibres during fabrication assembly. The silicon fibre network in a composite fabric is electrically conductive and can thereby be used to selectively

heat up intersecting polymer fibres to form a more rigid mated lattice.

Knitting is a continuous single element technique illustrated for example in Figure 3 hereinafter, in which a series of loops are interlocked vertically through the repetition of knitting stitches retained on some kind of tool or frame. The tensile strength of knitted fabrics is usually inferior to that from weaving but their flexibility and stretchability is greater.

Braiding is a process that utilises simple interlacing of a single set of elements with out any type of link, loop, warp or knot. It is differentiated from weaving by the warp serving as the weft, and by interlacing being in a diagonal or generally oblique pattern. Braiding is frequently called plaiting, webbing or interlacing.

Fibre bonding is a technique commonly used in the production of large-volume health products where fibre-to-fibre mating is generated by heat or solvents.

Air-laying and wet-laying are techniques suitable for forming fabrics from very short fibres. In air laying, the fibres are fed into an air stream before being deposited on a moving belt or perforated drum to form a soft web structure of randomly oriented fibres. Similarly wet-laying uses a mixture of fibres and water, which is deposited on a moving screen before being drained to form a web, consolidated between rollers and allowed to dry.

Finally, laminating is a way of joining of one fabric to another using an adhesive.

Alternatively, silicon and particularly amorphous or polysilicon may be coated onto a pre-existing fabric, for example by sputtering or continuous vapour deposition (CVD). Suitable fabrics may comprise any of the known fabrics, but in particular is a biocompatible fabric such as cotton, linen or a

biocompatible synthetic fabric such as polyester gauze as described above. Once coated in this way, the resultant silicon coating may optionally be porosified by stain etching as is known in the art, and described above.

5

Any or all of these techniques can be applied in the production of fabrics used in the present invention. Their applicability in any particular case depends upon the nature of the silicon fibres being used, and the requisite properties of the final fibre or fabric product.

10

Factors which need to be taken into account when selecting the type of fibre required in any particular case, and the technique used to convert this to a fabric include stress, strain, tensile fracture strength, malleability, and work of fracture.

15

Stress is simply load per unit area (units of N/m<sup>2</sup> or Pa). Strain is simply the amount of stretch under load per unit length (a ratio). Different materials are stretched/compressed by enormously varying degrees by extending/compressive forces. The corresponding ratio stress/strain, the Young's modulus (units of N/m<sup>2</sup> or Pa) thus describes the "stiffness" or elastic flexibility. It varies from 7Pa for rubber, 1.4kPa for most plastics, 2MPa for steel to about 1.2GPa for diamond.

25

Tensile fracture strength is the stress needed to break/fracture a material (N/m<sup>2</sup> or Pa) by stretching it. It also varies considerably about 4MPa for ordinary concrete, 50MPa for plastics to 2GPa for steel. Some values for materials used in fabrics are 40MPa (leather), 350MPa (cotton and silk). For brittle materials, fracture strength, FS, is controlled by critical flaws and given by the Griffith equation;

35

$$FS = (2VE/\pi c)^{0.5}$$



Where  $E$  is the Young's modulus,  $2V$  is the fracture energy required to form two new surfaces and  $c$  is the critical flaw size.

- 5 Malleability refers to the extent to which a metal can be manipulated before it breaks.

Work of fracture is the total energy needed to generate a fracture structure ( $\text{J/m}^2$ ). For ductile materials like copper  
10 and aluminium, values range between  $10^4$  and  $10^6 \text{ J/m}^2$ , much higher than the free surface energy.

The introduction of porosity makes a material more flexible (lowered Young's modulus) but also makes it weaker (lowered  
15 fracture strength). For brittle materials strength is limited by critical surface flaws which initiate crack propagation and fracture. Although textile materials generally comprise non-porous fibres, there are examples of fabrics that contain nanometre size pores. One such material is HPZ ceramic fibre  
20 where porosity is 20%, average pore width is 1.4nm. Single crystal "bulk" silicon has a Young's modulus of 162 GPa and a fracture strength of 7GPa. The introduction of mesoporosity in p+ silicon has been shown to significantly decrease Young's modulus according to the equation;

25 
$$E = (120 \times p^2) \text{ GPa}$$

where  $p$  is the relative density in the range 0.1 to 0.7, corresponding to 90 to 30% porosity. Values as low as 1GPa can be achieved in high porosity material.

30 Micromachined silicon structures will generally have the mechanical properties of bulk silicon prior to their porosification. However, silicon fibres, like glass fibres, get significantly stronger when the diameter drops below 5  
35 micron.

For glass the important defect is usually the surface crack. In a brittle crystal like silicon however, surface steps can

act as initiators of crack propagation by locally increasing stress. Thus it may be preferable to reinforce the surface of the silicon fibres used in the invention, for example by resin bonding.

5

Polycrystalline silicon may be used in the invention, and therefore whenever the term "silicon" is used herein, it may include this form. Polycrystallinity does not lower strength provided the surface energy of the grain boundaries exceeds  
10 that of the crystal fracture planes.

15

Similarly amorphous silicon may be biologically acceptable or bioactive, and therefore whenever the term "silicon" is used herein, it may include this form unless specified otherwise.

20

To achieve sufficient flexibility for use in medical fibres and fabrics, non-porous silicon fibres are suitably less than 50 micron in diameter. Porosifying part of the fibre will improve flexibility at a given diameter but decrease strength.

25

A partially porous silicon fibre will not be fully biodegradable but could have substantially greater strength, and thus be preferable in certain situations.

30

In order to avoid the surface failure mechanisms discussed above, introducing porosity into the fibre core rather than at the surface coating would be preferable in order to improve strength. This could be realized by selective anodising of a p<sup>++</sup>/n<sup>-</sup> fibre or poly-Si coating of a wholly porous fibre or  
30 partial sintering of a wholly porous fibre.

Fabrics prepared from substantially pure silicon fibres are novel and form a further aspect of the invention.

35

In yet a further aspect, the invention provides a process for preparing a medical fabric, which process comprises weaving, knitting, embroidering or fibre bonding substantially pure silicon.

Fibres and fabrics constructed from silicon or silicon composites may be semi-conducting. Thus the invention further provides an electrically conductive silicon or silicon composite fibre or fabric. Such fibres and fabrics are particularly useful in medical applications since the semiconducting nature allows for good distribution of electrical charge, where these are used in therapy. A particular form of such a fabric is a silk based fabric which comprises silk warp threads and low resistivity silicon containing weft threads.

Thus in a further aspect the invention provides a method for enhancing tissue growth, which method comprises applying to a patient in need thereof, a semiconducting fabric comprising silicon, and passing controlled levels of electrical current through said fabric.

Fibres and fabrics as described above have a variety of medical applications. For example, fabrics which have large pores (>100 micron) for cellular infiltration can be used as scaffolds for tissue engineering. The use of the different fabrication techniques listed above provides for exceptional flexibility of 2D topography.

They may also be of use in orthopaedic prostheses where the mesoporosity of the fibres provides bioactivity whilst the macroporosity of the textile pattern directs and allows bone in-growth.

The electrical conductivity of the textile is also of benefit in orthopaedic applications where osteogenesis is controlled by application of distributed electrical charge. Invasive bone growth stimulators that utilise a wire mesh cathode are currently used in spinal fusion.

A stent is a mesh-like collar designed to serve as a temporary or permanent internal scaffold to maintain or increase the lumen of a vessel. Essential stent features include radial and

torsional flexibility, biocompatibility, visibility by X-ray and reliable expandability. It is an example of a widely used implant that is currently engineered from malleable but non-biodegradable materials such as metals. A silicon or silicon  
5 containing fabric as described above, may form the basis of these stents. Particular preferred fabrics would comprise biodegradable forms and partially porous forms for eluting drugs locally. These forms would be possible using fully or partially porous silicon fibres as described above, in the  
10 production of the stents.

A further possible application for the fabrics described above is in flexible electrodes for neuro-interfacing. The macroporosity of the fabric enables tissue in-growth. In  
15 addition, the fibres used are preferable at least partially mesoporous, which means that they offer lower impedance. In order to ensure the very high electrical conductivity and stability which is important in such devices, in this case, it may be preferable to use fibres comprising a non-porous heavily  
20 doped silicon core, with a porous silicon layer that has been electroplated with an ultrathin conformal coating of a metal such as platinum or iridium.

The fabrics described above could also be used to produce  
25 "wrapped" in-vivo drug delivery systems. For instance, they may be used in the localised delivery to curved areas of an organ or for the encapsulation of drug-eluting cells. In these cases, biocompatibility of the composite formulation is essential.

30 In a variant on this application, they may be used in "wrapped" ex-vivo drug delivery systems. In this case, it may be preferable to use a fabric that is augmented with drug-eluting pSi particles that dissolve in sweat. In such cases, the core  
35 fabric need not be biodegradable and is a medical fabric only to the extent that it does not irritate the skin.

An extension of such applications may include textiles wherein the silicon within the fibres or fabrics is impregnated with drugs to treat the skin for dermatological conditions, which can be incorporated or comprised within dressings applied  
5 directly to the skin. In addition, such fibres and fabrics can be used for localised topical delivery of drugs used to treat conditions such as anti-inflammatory drugs, used to treat arthritic joints for instance.

10 Passive drug diffusion through the skin could be used in particular where small molecules like silicic acid are being diffused. Semiconducting fabric as described above might be used in an iontophoresis-type design for transdermal delivery of large biomolecules.

15 The electrically conducting properties of the fabrics described above makes them suitable for distributed networks for electrical stimulation. In these applications, a fabric is wrapped around a target area and can be used to electrically  
20 stimulate an array of sites simultaneously

Non-occluding garments, or other wearable structures such as patches or bandages, for sweat diagnostics may also incorporate the fabrics described above. Here the fabric used, in  
25 particular for non-occluding garments, may be one with a relatively open lattice as this helps maintain normal hydration levels of skin and flexibility compared to the silicon chips currently used for this process. It also enables vastly increased area coverage. The widely distributed porous Si  
30 component acts as a large clean reservoir for collecting excreted biochemical markers.

A relatively cheap garment (e.g. teeshirt plus porosified metallurgical grade particulate polysilicon) may be employed as  
35 a one-shot sweat collection device for analysis after strenuous physical exercise.

Reservoir particles can be removed from the fabric of the garment or the like, after wear and sweat incorporation by extended sonication. Markers collected within the mesopores are then subjected to standard analysis techniques after  
5 solvent extraction. Biochemically stable silicon particles, which are preferably derivitised by techniques described in WO 00/006190, are suitably included in the garments.

The semiconductive nature of the fabric also facilitates  
10 enhanced sweating via electrical elevation of skin temperature. Joule heating of the silicon microfibres in particular in a bandage or patch like structure can locally raise temperature to a sufficient level to promote sweat production and collection. Again this can be recovered subsequently from  
15 reservoir particles of porous silicon. However, this may be applied more widely where localised heating of the skin is required. In that case, the silicon used may or may not be porous, provided the fabric is semiconducting in nature.

20 A method of collecting sweat using this technique, as well as a method of locally heating skin forms particular embodiments of the invention.

Hollow silicon containing fibres as described above, may  
25 suitably be employed to form fabrics for use in flexible immuniosolation networks. In this case, foreign cells used are housed in central channels of hollow mesoporous fibres. Suitably the fabric has a relatively open architecture, which encourages vascularisation around every fibre.

30 The porous nature (both macroporous and mesoporous) of the silicon containing fabrics described above may be utilised in wound repair, for example to deliver drugs such as antibiotics. Thus these fabrics may be used in absorptive dressings. Also  
35 polycrystalline silicon may be particularly useful in fabrics used to facilitate wound repair.

Yet a further specific application of the silicon containing fibres described above is in the production of X-ray opaque yarns. Silicon is relatively opaque to X-rays and therefore could be used instead of the current polymers, which must  
5 contain at least 50% by weight of barium sulphate to render them sufficiently opaque to be used as markers in surgical swabs or sponges.

Where the fibres or fabrics discussed above include porous or  
10 non-porous silicon, this opens up the possibility that they may be used for slow release of a variety of substances. As well as pharmaceuticals or drugs, they may include fragrances and the like. Particular examples of such substances are essential oils, which may be fragrant and/or may have a therapeutic  
15 effect.

Thus the present invention is particularly advantageous since it allows fibres and fabrics to be produced with the desired combined biodegradability and mechanical properties for a wide  
20 variety of application. The semiconducting nature of the silicon used allows for the possibility of distributing electrical charge in a medical context. Furthermore, in the case of the fabrics, the desirable effects of dual porosity (i.e. micro or meso porosity of the fibres themselves as  
25 produced for example by electrochemical etching, and macroporosity determined by selection of weave design) can be achieved, so that for example bioactive open meshes can be produced for bone in-growth and other complex 2D and 3D topographies achieved depending upon the intended end use.

30 The invention will now be particularly described by way of example, with reference to the accompanying drawings in which:

Figure 1 illustrates diagrammatically the structure of woven  
35 fabrics,

Figure 2 illustrates diagrammatically the structure of yarns,

Figure 3 illustrates diagrammatically the structure of knitted fibres,

Figure 4 shows microscope images of porous c-Si microfibres of  
5 smallest widths (a) about 100 micron (x200) (b) about 25 micron  
and (x200) (c) an elastically bent 100 micron wide fibre (x20),

Figure 5 shows microscope images of (a) a partially sawn wafer  
(x 3) (b) a sawn silicon beam array (x 32) and (c) an etched  
10 silicon beam array (x 100),

Figure 6 shows a microscope image of a porous c-Si microfibre  
of smallest width (a) 20 micron (b) 4 micron, and (c) a  
multistrand fibre (scale and magnification shown),  
15

Figure 7 shows microscope images of woven c-Si structures with  
(a) a 200 micron thick warp & weft and (b,c) 100 micron thick  
warp and 300 micron thick weft (scale shown),

20 Figure 8 shows microscope images of polyester gauze coated with  
10 micron thick layer of semiconducting silicon (scale shown),

Figure 9 shows SEM images of view of the surface of the  
polyester gauze after coating (a,b), and the corresponding  
25 Energy Dispersive X-ray (EDX) spectrum, (scale shown)

Figure 10 is an enlarged view of polyester gauze fibres after  
stain etching (a,b) (scale shown) and (c) the EDX spectrum of  
the fibres,  
30

Figure 11 shows a scanning electron microscope image of a  
silicon coated (a) biodegradable suture (b) aluminium wire and  
(c) hollow glass fibre, (scale shown) and

35 Figure 12 is an enlarged view of a coated suture and fibre  
illustrating the retained flexibility of the structure (scale  
shown).



Example 1Preparation of Extruded poly-Si fibres and fabrics obtained therefrom

Poly Si microwires of diameter 5-25 micron diameter are first  
5 made by the "Taylor microwire process". Here, a poly or  
metallurgical grade silicon charge is melted inside a glass  
tube by a local heating source and fine wire drawn out through  
an orifice by mechanical pulling. The wire so produced is  
sheathed in silica which is removed by HF-based treatment.

10

The wires are then woven, knitted or braided into appropriate  
design prior to porosification in a HF-based solution. For 5-  
10 micron diameter wires, full porosification is achievable  
with stain-etching techniques. Anodisation of fabric made from  
15 low resistivity poly/single crystal silicon could alternatively  
be used, especially for thicker fibre networks.

Example 2Preparation of Reinforced silicon fibres

20 Bundles of silicon composite fibres, prepared for example as  
described in Example 1, can be processed into much tougher  
forms using resin bonding techniques used to convert highly  
brittle glass into extremely tough fibreglass. Although the  
resin used in fibreglass may itself be brittle, the interface  
25 between the silicon and the resin (as with the glass-resin  
interface) will act as an effective barrier to crack  
propagation across the bundle.

Example 3Preparation of Extruded polymer/Si powder fibres

A readily extrudable polymer is first blended with porous  
silicon powder to form a composite that can still be processed  
into fibres at moderate temperatures. The level of silicon  
incorporation is between 1-10wt% for inducing bioactivity, 10-  
35 60wt% for improving yield strength and 60-90wt% for conferring  
electrical conductivity to an insulating polymer, for example.

When a biodegradable polymer such as polylactic glycolic acid (PLGA) is used, the composite textile retains biodegradability.

When an established textile material such as Dacron™ is used, the inclusion of pSi powder can be incorporated as one

- 5 additional step in a commercial sequence. Where electrically conducting polymers such as polyaniline or polyacetylene are used, textiles obtained are not biodegradable but could be rendered surface-bioactive by low levels of silicon addition.

10 Example 4

Preparation of Hollow amorphous/polysilicon microfibrs

- Commercially available polymer/silica fibres of diameters in the range 20-200 micron with a hollow core of diameter in the range 5-100 micron is first coated along its length with
- 15 amorphous/poly silicon. This can be achieved by pulling the fibre through a vacuum sputtering/CVD chamber and with deposition at room temperature/elevated temperature respectively. The low thermal stability of polymers restricts their coating to amorphous films which can be carried out at
- 20 room temperature. The core of the fibre is then removed by soaking in a suitable solvent/HF-based solution.

- Porosification can once again be by stain etching or anodisation. Since microcracks limit fibre strength, improved
- 25 drying techniques like supercritical processing are beneficial.

Example 5

Preparation of Micromachined poly-Si fibres

- Ultrathin fibres can be realised by the repetitive use of
- 30 standard silicon wafers that are repetitively subjected to surface oxidation, poly-Si deposition, micromachining and HF-induced release. Porosification is carried out by stain etching either before or after the HF-release step. The maximum fibre length is defined by wafer diameter and fibre
- 35 cross-section by poly-Si layer thickness and mask design.

Example 6Silicon incorporation into preformed fabric

Commercially available silicon powder (metallurgical grade or solar grade purity) is mechanically milled down to submicron particle size and then rendered porous by stain etching in an HF-based solution. The porous powder is then subjected to UV ozone treatment to generate surface hydroxyl groups. Their replacement by 3-chloropropyl (CP) groups is then achieved by using (3-chloropropyl) trimethoxysilane (CP-TMS). Covalent binding via propyl ether linkages to commercially available fabric, such as cotton, linen or a synthetic fibre, is then achieved by co-incubation in boiling toluene. After sufficient reaction time (e.g. 2 hours at 110°C) sonification can be used to remove physisorbed pSi powder, leaving only covalently linked silicon powder bound to the surface of the fabric.

Example 7Silicon Incorporation into Preformed Yarn

Non porous or porous silicon fibre prepared by the process described in Examples 1 or 5 is wrapped around textile fibres that have already been spun into yarn. This can provide an electrically conductive pathway within a fibre of predominantly standard textile material.

Example 8Metal replacement by silicon in silk organza

Silk organza is a finely woven silk fabric, originating from India, which combines gold, silver or copper with silk threads into a fabric that is anisotropically conductive. The warp consists of parallel silk threads. Through this warp, the weft is woven with a silk thread that has been wrapped in a metal foil helix.

In this embodiment however, low resistivity silicon fibres are used instead of the foil wrapped fibres. The spacing between the fibres results in a correctly orientated strip of the fabric functioning like a ribbon cable.

Example 9Preparation of porous silicon fibre

Porous silicon fibre was obtained by cleaving a mesoporous film on wafers over a glass slide covered in filter paper. An 80%  
5 porosity and 64 micron thick film was fabricated from a (100) oriented p+ wafer ( $0.005 \pm 20\%$  ohm cm) made by anodisation at 100 milliamps per square centimetre, for 20 minutes in equal volumes of 40wt% HF and pure ethanol. Upon scribing the back of the wafer along directions parallel or perpendicular to the  
10 "wafer flat" and then breaking over the aligned edge of a glass slide, some short (1-10 mms) fibres broke away from the diced chip. Examples are shown in Figure 4 which show optical microscope images at x200 magnification of fibres of rectangular cross-section (a) 95-100 micron width (b) 25-30  
15 micron width. The fibrous structures are fully porous (80% porosity) and brown to the eye. Figure 4(c) is another optical microscope image of the larger fibre bent on a carbon pad to illustrate its flexibility.

20 Example 10Preparation of porous silicon fibre

In an alternative method, porous silicon fibre was obtained by etching and anodisation of sawn silicon comb-like structures like that shown in Figure 5(a). The edge of a 3 inch diameter  
25 wafer was given a series of 45 cuts using a 75 micron wide blade with a pitch of 225 micron. This created an array of supported single crystal beams of approximate length 12mms and rectangular cross-section 150x380 micron.

30 These beams were then subjected to ultrasonic cleaning in acetone and then an isotropic wet etch in 70% nitric acid, glacial acetic acid and 40% aqueous HF at a 5:1:1 volume ratio. This step removes saw damage and is used to define cross-sectional profile of fibres to be generated in the next step.

35 The etching solution was continuously stirred and etch duration was 7.5 minutes for the data shown here. Figure 5(b,c) shows the beam array in plan-view before and after such an etch where the width has been reduced from  $145 \pm 5$  micron to  $25 \pm 5$

micron. The wafer segment was then further cleaved into a narrower comb-like structure with no bulk silicon adjacent to the ends of the protruding beams, in preparation for anodisation. An anodic potential of 1.0 Volt was applied for 5 minutes in 40% aqueous HF/ethanol (1:1 by volume) between the suspended structure and a circular platinum crucible acting as the cathode. Only the lower half of the beams were immersed in the electrolyte. The resulting high current densities caused the pSi films to delaminate as fibres of uniform width defined by beam dimensions and anodisation time.

As an alternative, it would be possible to initially apply low current densities and then a sufficiently high current density to cause "lift-off", as is well known in the production of pSi membranes from whole wafers.

Figure 6(a-c) show examples of a 20 micron wide, a 4 micron wide and the end of a multistrand fibre respectively, obtained using this method. As a result of the anodisation conditions used, the porosity of these wholly porous structures is in excess of 60%.

#### Example 11

##### Preparation of woven silicon structures

The sawing and etching process described above was used to demonstrate the feasibility of weaving pure silicon fibres using larger structures. Square sections of wafers were sawn into comb-like structures and given etch treatments to reduce thickness to 300, 200 and 100 microns over much longer lengths.

Figure 7(a) shows an example of a pure single crystal Si weave where both warp and weft fibres have 200 micron thickness. Figure 7(b,c) shows a Si weave containing weft fibres of 300 microns and warp fibres of 100 microns thickness. The latter have a pSi coating derived by stain etching as described in Example 12 hereinafter, which gives them a brown colour to the eye.

Example 12Preparation of Si & porous Si coated fabrics, sutures and threads

A range of fibrous materials were conformally coated with sputtered amorphous silicon in a modified Blazers Bak box coater equipped with four, 400x125mm planar magnetrons arranged concentrically around a central substrate rotation stage. Coating was by sputtering from a 99.999% pure Si target doped with boron at  $5 \times 10^{18}/\text{cm}^3$  with the target power set at 500W, a base pressure of  $10^{-8}$  torr, an ionisation atmosphere of  $5 \times 10^{-3}$  torr of argon and a substrate temperature of 50 C. The substrates were rotated at speeds of between 0.0025 and 0.126mm/sec and supported on a custom-built framework to improve uniformity and control thickness of coatings.

A commercially available polyester gauze (denier 100, mesh 156) was coated with 200nm, 1 micron and 10 microns of silicon. Figure 8(a,b) show segments of the gauze with the thickest coating and demonstrate the retained flexibility. The coatings were found to adhere well, even when tied into a knot as shown. Figure 9(a,b) shows SEM images of part of the coated gauze and Figure 9(c) the corresponding EDX spectrum showing a low level of oxygen in the coating.

All exposed surfaces of the multistrand fibre network were found to have such a Si coating. Figure 10(a,b,c) show the corresponding images and spectrum of the same gauze after partial porosification of the coating by stain etching. This was achieved by immersion of the fabric in a conventional stain etch solution containing 1 part by volume of 70% nitric acid to 100 parts by volume 40% HF for 60 seconds. A 90 second etch was found to cause partial delamination of the pSi coating. The porous nature of the coating is evident from the raised oxygen and fluorine levels in Figure 10(c) and the presence of some cracks in Figure 10(b).

Other examples of silicon coated structures include a biodegradable suture (the multifibre thread of Figure 11(a)), a

metal (aluminium) wire (Figure 11(b)), hollow glass fibre and tubes (Figure 11(c)) and other single strand polymer fibres. If desired, the glass or metal interior structures may subsequently be dissolved away using an appropriate solvent, such as hydrofluoric acid for glass, and hydrochloric acid for aluminium.

Figure 12 is an optical image showing the flexibility of the suture and polymer fibres are maintained after Si coating.

10

#### Example 12

#### Illustration of the semiconducting nature of medical fabrics comprising silicon

The woven pure silicon structure of Figure 7(a) was rendered partially mesoporous by application of anodic electrical bias in equal volumes of 40%HF and ethanol. During and following this process the structure remained semiconductive since porous silicon is itself semiconducting.

The gauze coated with porosified silicon of Figure 10 was cathodically biased in simulated body fluid. Prior to coating, the gauze is electrically insulating. Any current flow is thus restricted to the surface coating. This and the higher resistivity of the amorphous silicon compared with that of crystalline silicon resulted in a bias of 30 volts being needed to maintain a current flow of 1mA through the fabric.

The conductivity of the gauze can be raised by using a more heavily doped ( $10^{20}$  B/cm<sup>3</sup>) Si target in the sputtering process, or by rendering the Si coating polycrystalline by laser annealing.

#### Example 13

#### Preparation of Flexible Si chains of beads

Spherical polycrystalline Si granules of diameter 1-5mm are commercially available in kg quantities from MEMC Inc, USA. After mechanical sieving these are size separated to for example 1.0 mm diameter. A 500 micron diameter hole is then

drilled through each and batches given an isotropic chemical etch to remove drill damage. Subsequent linear alignment of holes is followed by threading, using a lead wire attached to the medical linking fibre. Partial porosification is achieved  
5 by stain etching or anodisation using a conducting Pt wire to link a chain of interconnected spheres.

#### Example 14

##### Preparation of Flexible Si chains of microbeads

10 A silicon wafer is thermally oxidised and a 150 micron thick Si membrane bonded to that oxide surface. A linear array of rectangular trenches are then deep dry etched to a depth of 50 microns into that Si coating and in-filled with a spun-on resist. This step defines what will become the hollow core of  
15 every bead.

Following surface planarisation and cleaning, another 100 micron thick Si membrane is wafer bonded to the array. Photolithographically defined deep dry etching right through  
20 the Si-resist-Si structure to a depth of 250 microns is then carried out in a linear array pattern orthogonal to the resist channel direction. This step divides the linear Si columns into rows of aligned particles. The resist channels are then leached out by solvent and a suitable microwire (<50 micron  
25 diameter) threaded through at least one chain of aligned particles running across the wafer diameter.

When the entire array is suitably threaded the wafer is immersed in HF to dissolve the underlying oxide and release the  
30 particle chains. Isotropic etching can be subsequently used to remove sharp particle edges and stain etching to porosify the surfaces of every particle in the chain.



## Claims

1. A fibre or fabric comprising silicon for use as a medical fibre or fabric.
- 5 2. A fibre or fabric according to claim 1 wherein the silicon is bioactive silicon.
3. A fibre or fabric according to claim 1 wherein the silicon  
10 is resorbable silicon.
4. A fibre or fabric according to claim 1 wherein the silicon is biocompatible.
- 15 5. A fibre or fabric according to any one of the preceding claims wherein the fibre or fabric is a semiconductor.
6. A fibre or fabric according to any one of the preceding claims wherein the silicon is porous silicon.  
20 7. A fibre or fabric according to claim 6 wherein the silicon is mesoporous silicon.
8. A fabric according to any one of the preceding claims,  
25 wherein the fabric has silicon microparticles incorporated therein.
9. A fabric according to claim 8 wherein the silicon microparticles are covalently bound to fibres of the fabric.  
30 10. A fibre or fabric according to any one of claims 1 to 7 which is a fibre and the fibre is formed of silicon.
11. A fibre or fabric according to any one of claims 1 to 7  
35 which is a fibre and the fibre comprises a composite with another material.

12. A fibre or fabric according to claim 10 or claim 11 wherein the fibre is formed into a fabric.
13. A fabric according to claim 12 which contains only silicon  
5 containing fibres.
14. A fibre or fabric according to claim 12 wherein the fabric comprises fibres other than silicon containing fibres.
- 10 15. A fibre or fabric according to any one of claims 12 to 14 wherein fabric is obtained by spinning, embroidery, weaving, knitting, braiding, fibre bonding, air-laying, wet laying, and/or laminating fibres.
- 15 16. A fabric having silicon microparticles incorporated therein.
17. A fabric according to claim 16 where the silicon microparticles are covalently bound to the fabric.
- 20 18. A porous or partially porous silicon containing fibre.
19. A fibre according to claim 18, which is a porous silicon fibre.
- 25 20. A method of preparing a fibre according to claim 19 which method comprises mechanically cleaving a mesoporous film on a silicon wafer.
- 30 21. A method of preparing a fibre according to claim 19 which method comprises forming a silicon fibre and thereafter porosifying the silicon.
22. A method according to claim 21 wherein the silicon fibre  
35 is formed by melt pulling, Laser-assisted chemical vapour deposition (LCVD), VLS methods, coating of sacrificial fibrous material or micromachining.

23. A method according to claim 21 or claim 22 wherein the silicon fibre is porosified by anodisation or stain etching.
24. A fabric comprising fibres according to claim 18 or claim 19.
25. A method for preparing a fabric according to claim 24 which comprises spinning, embroidery, weaving, knitting, braiding, fibre bonding, air-laying, wet laying, and/or laminating fibres according to claim 18 or claim 19.
26. A substantially pure silicon fibre of at least 100cm in length.
27. A fabric comprising a fibre according to claim 26.
28. A fibre according to claim 26 or a fabric according to claim 27 wherein the silicon is porous silicon.
29. A method for preparing a fabric according to claim 27 which comprises spinning, embroidery, weaving, knitting, braiding, fibre bonding, air-laying, wet laying, and/or laminating fibres according to claim 18, claim 19 or claim 26.
30. A method for producing a fibre comprising silicon, which method comprises coating a microfibre with silicon or a silicon composite.
31. A method according to claim 30 wherein the microfibre is a biodegradable suture.
32. A method according to claim 30 wherein the microfibre is soluble and wherein in a subsequent step, said microfibre is wholly or partially dissolved to producing a hollow amorphous silicon or silicon composite microfibre.
33. A method according to claim 32 wherein the said soluble microfibre is hollow.

34. A method according to any one of claims 30 to 33 wherein the silicon microfibre obtained is porosified.

35. A fibre or fabric according to any one of claims 1 to 17  
5 wherein the silicon containing fibres are reinforced by resin bonding.

36. A fibre or fabric according to any one of claims 1 to 17  
or claims 35 wherein the fibres or the fibres used in the  
10 fabric are less than 50 micron in diameter.

37. A silicon containing fibre having a porous core and a non-porous coating.

15 38. A fibre according to claim 37 which is a pure silicon fibre.

39. A process for preparing a medical fabric, which process comprises weaving, knitting, embroidering or fibre bonding pure  
20 silicon fibres.

40. A process for preparing a silicon fabric, which process comprises cutting a first and a second silicon wafer to form a series of parallel cuts therein, and interweaving the resultant  
25 silicon threads in a substantially perpendicular direction.

41. A process according to claim 40 wherein the cut fibres are subject to cleaning and/or etching before or after interweaving.  
30

42. A process according to claim 40 or claim 41 wherein the silicon threads are porosified before or after interweaving.

43. A process according to claim 42 wherein the silicon  
35 threads are porosified after interweaving.

44. A method of preparing a silicon coated fabric, which method comprises coating a fabric with silicon.

36.

45. A method according to claim 44 wherein the coating is effected by sputtering or continuous vapour deposition.

46. A method according to claim 44 or claim 45 wherein the resultant silicon coating is porosified.

47. A silicon coated fabric obtainable by a method according to any one of claims 44 to 46.

48. An electrically conductive silicon or silicon composite fibre or fabric.

49. A fibre or fabric according to claim 48, which comprises silk warp threads and low resistivity silicon containing weft threads.

50. A silicon fibre comprising silicon beads connected together by means of a resilient thread or wire.

51. A silicon fibre according to claim 50 wherein said resilient thread or wire is a biodegradable suture.

52. A silicon fibre according to claim 50 or 51 wherein the silicon beads are of from 0.5 to 5mm in diameter.

53. A silicon fibre according to claim 50 or claim 51 wherein the silicon beads are from 10-500 microns in diameter.

54. A silicon fibre according to any one of claims 50 to 51 wherein the silicon beads are porous.

55. A method for preparing a silicon fibre according to claim 50, claim 51 or claim 52, which method comprises drilling holes through silicon granules, and passing a resilient thread or wire through the holes formed in a plurality of granules.

56. A method for preparing a silicon fibre according to claim 50, claim 51 or claim 53, which method comprises forming a plurality of beads with a central cavity on a dissolvable surface by photolithography, introducing a resilient thread or  
5 wire through cavities in said plurality of beads, and thereafter dissolving said surface.

57. A method according to claim 56 wherein the dissolvable surface is a silicon oxide surface, formed on a silicon wafer.  
10

58. A method according to claim 56 or claim 57 wherein the plurality of beads are formed by depositing a silicon membrane on said dissolvable surface, etching an elongate trench into said surface, applying a further silicon membrane to said  
15 surface, and then etching channels both perpendicular to and parallel to said trench.

59. A method for enhancing tissue growth, which method comprises applying to a patient in need thereof, a  
20 semiconducting fabric comprising silicon, and passing controlled levels of electrical current through said fabric.

60. A medical device comprising a fibre or fabric comprising silicon.  
25

61. A medical device according to claim 60 which is selected from a scaffold for tissue engineering, an orthopaedic prostheses, a stent, an electrode for neuro-interfacing, a "wrapped" in-vivo drug delivery system, a "wrapped" ex-vivo  
30 drug delivery system, a medical distributed network for electrical stimulation, a non-occluding garment, patch or bandage for sweat diagnostics, a topical dressing which is optionally absorptive, or an X-ray opaque yarn.

35 62. A substantially pure silicon yarn.

63. A silicon containing yarn.

64. A silicon containing yarn according to claim 63 wherein one or more pure silicon fibres are intertwined with textile fibres.

5 65. A fibre or fabric comprising porous silicon, wherein the silicon is impregnated with a substance such that the substance is slowly released from the silicon.

66. A fibre or fabric according to claim 65 wherein said  
10 substance is a pharmaceutical compound or a fragrance.

67. Use of a fibre or fabric containing silicon as a medical fibre or fabric.

15 68. Use according to claim 67 wherein the medical fibre or fabric is a suture, threads or mesh for medical application.

69. A method for collecting sweat from an individual, said method comprising applying to the skin of the individual a  
20 fabric comprising porous silicon, and later recovering the contents of pores within the silicon.

70. A method according to claim 69 wherein the fabric is in the form of a patch or bandage.

25

71. A method according to claim 69 or claim 70 wherein the fabric is semiconducting as a result of the presence of the porous silicon, and a current is applied to locally heat the skin in the region of the fabric so as to promote sweating in  
30 this region.

72. A method of locally heating the skin of an individual, said method comprising applying to the skin a semiconducting fabric comprising silicon, and applying a current through the  
35 fabric.

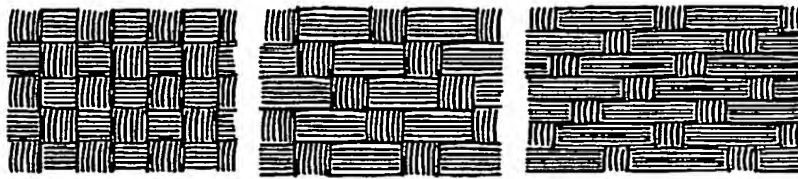


Fig. 1

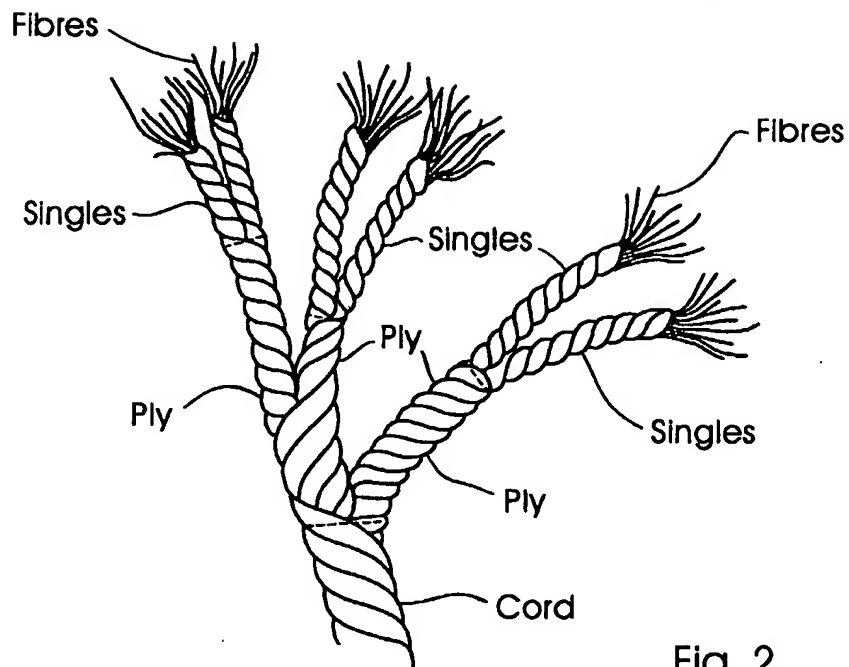


Fig. 2

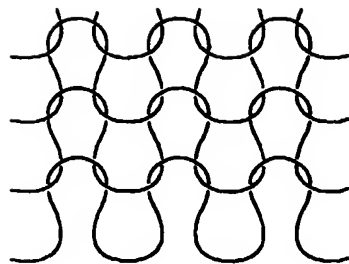


Fig. 3a

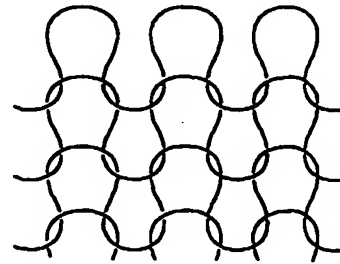


Fig. 3b



2 / 15



Fig. 4a



Fig. 4b



Fig. 4c

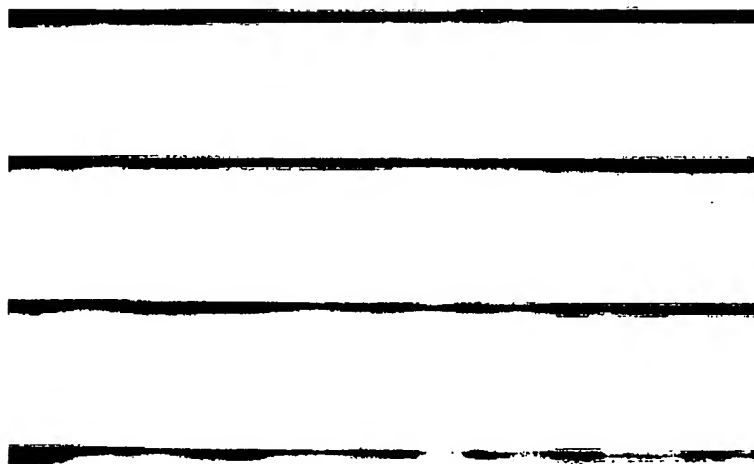


Fig. 5c

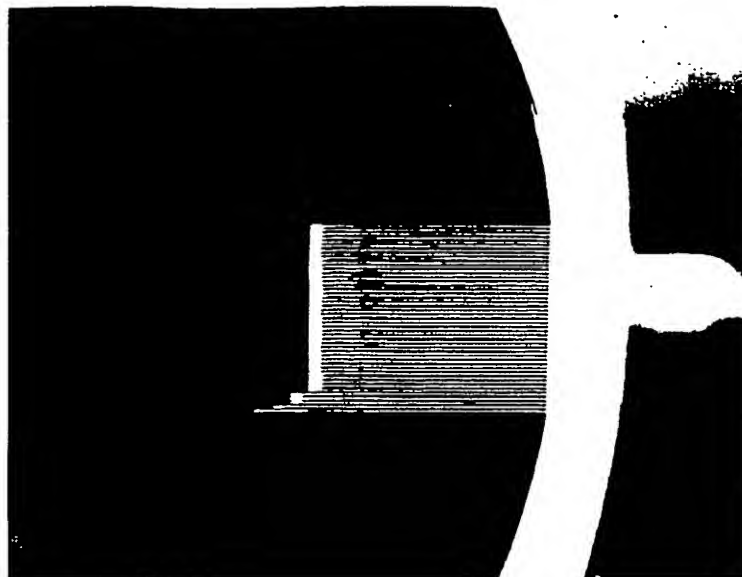


Fig. 5a

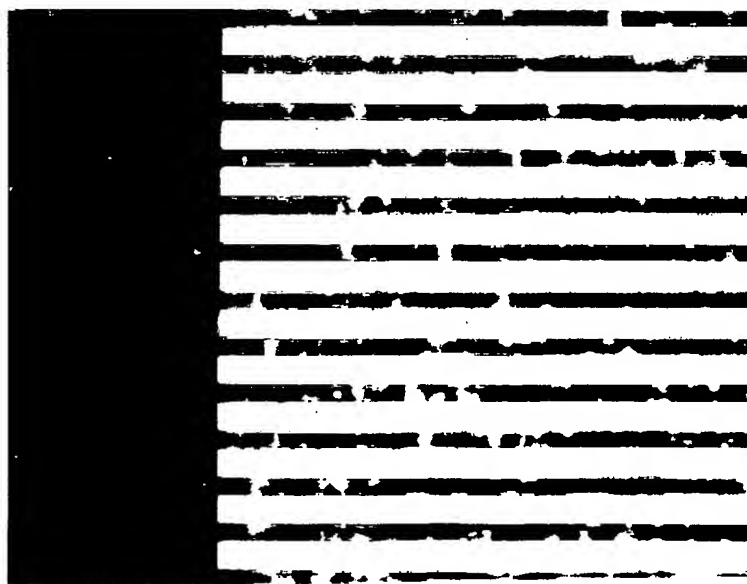


Fig. 5b

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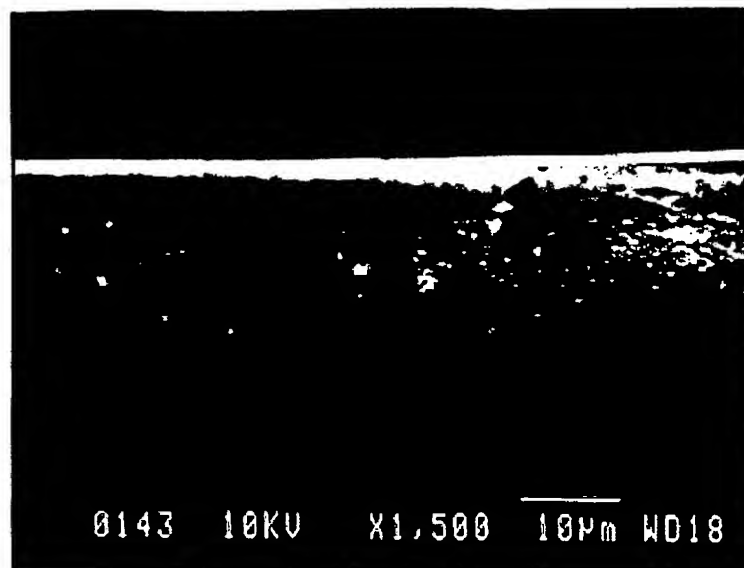


Fig. 6a

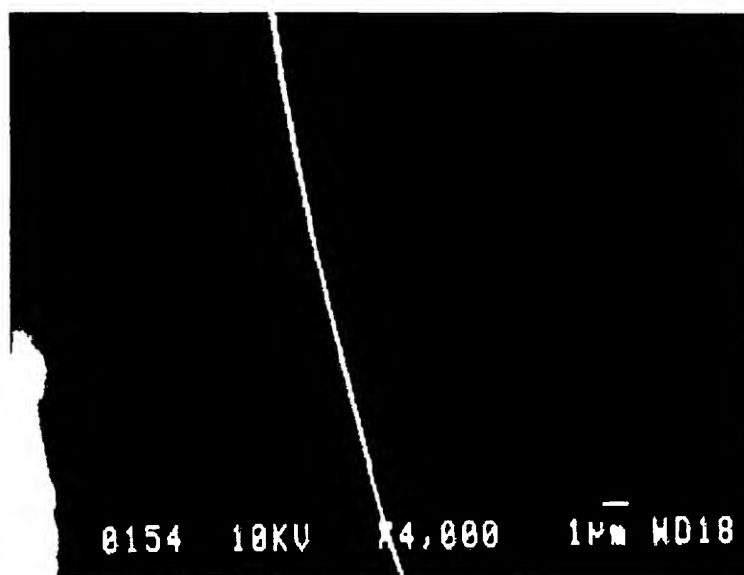


Fig. 6b

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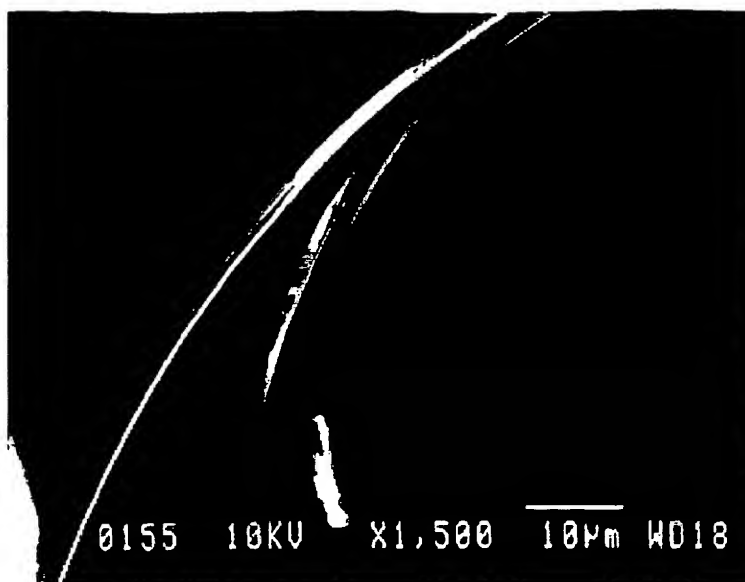


Fig. 6c

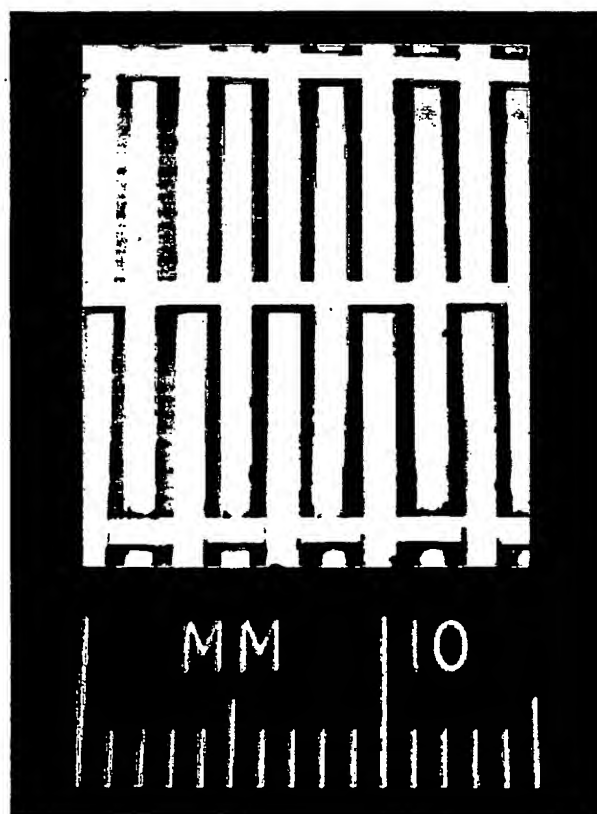


Fig. 7a

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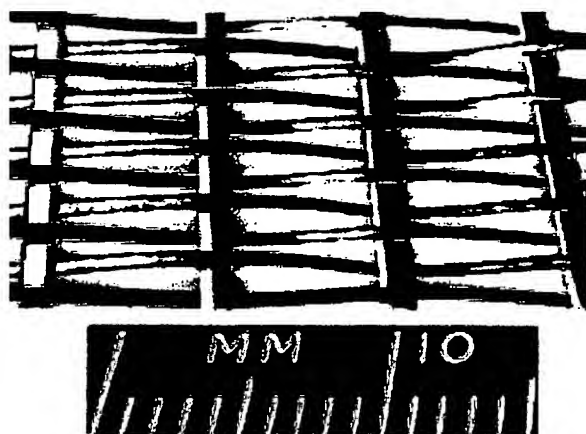


Fig. 7b

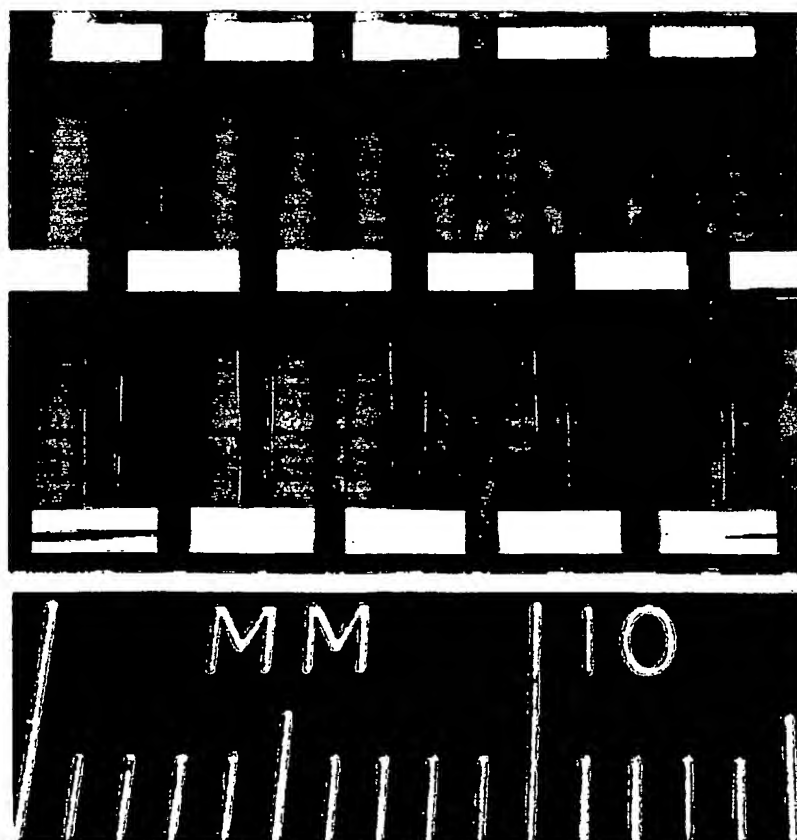


Fig. 7c

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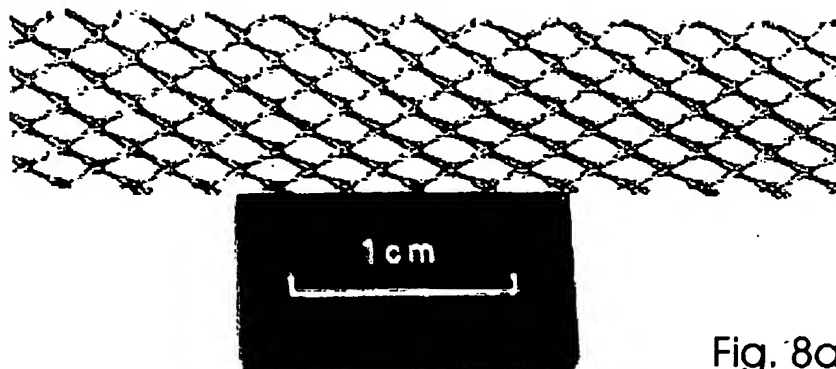


Fig. 8a

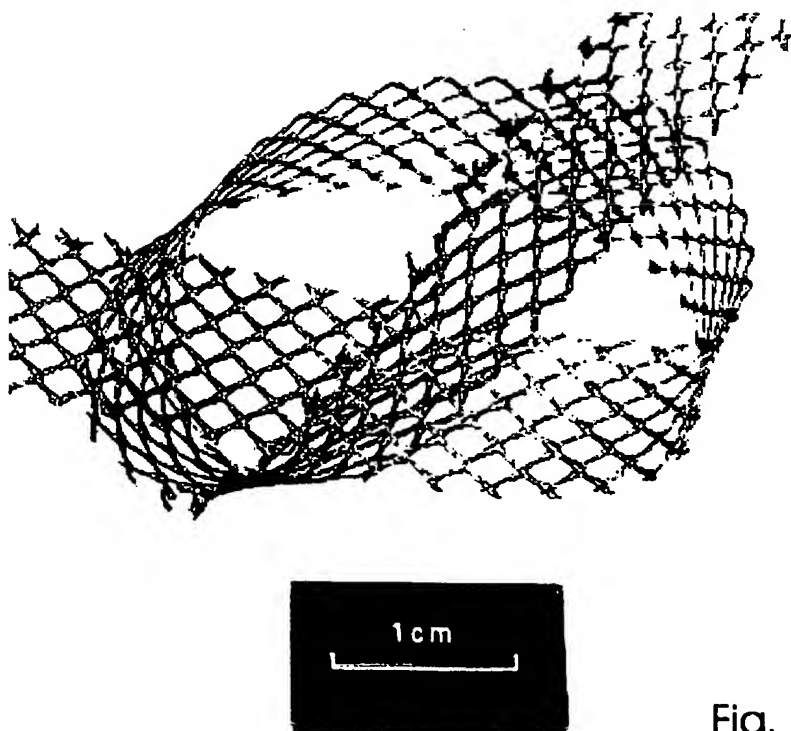


Fig. 8b

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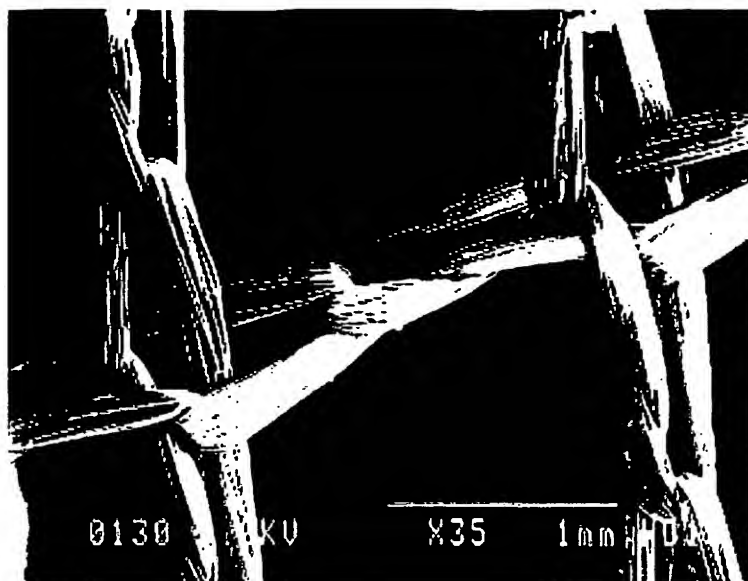


Fig. 9a

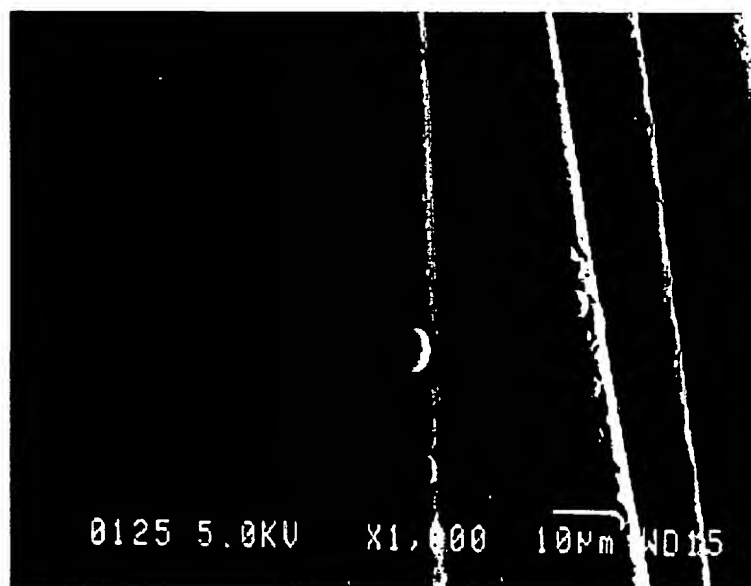


Fig. 9b



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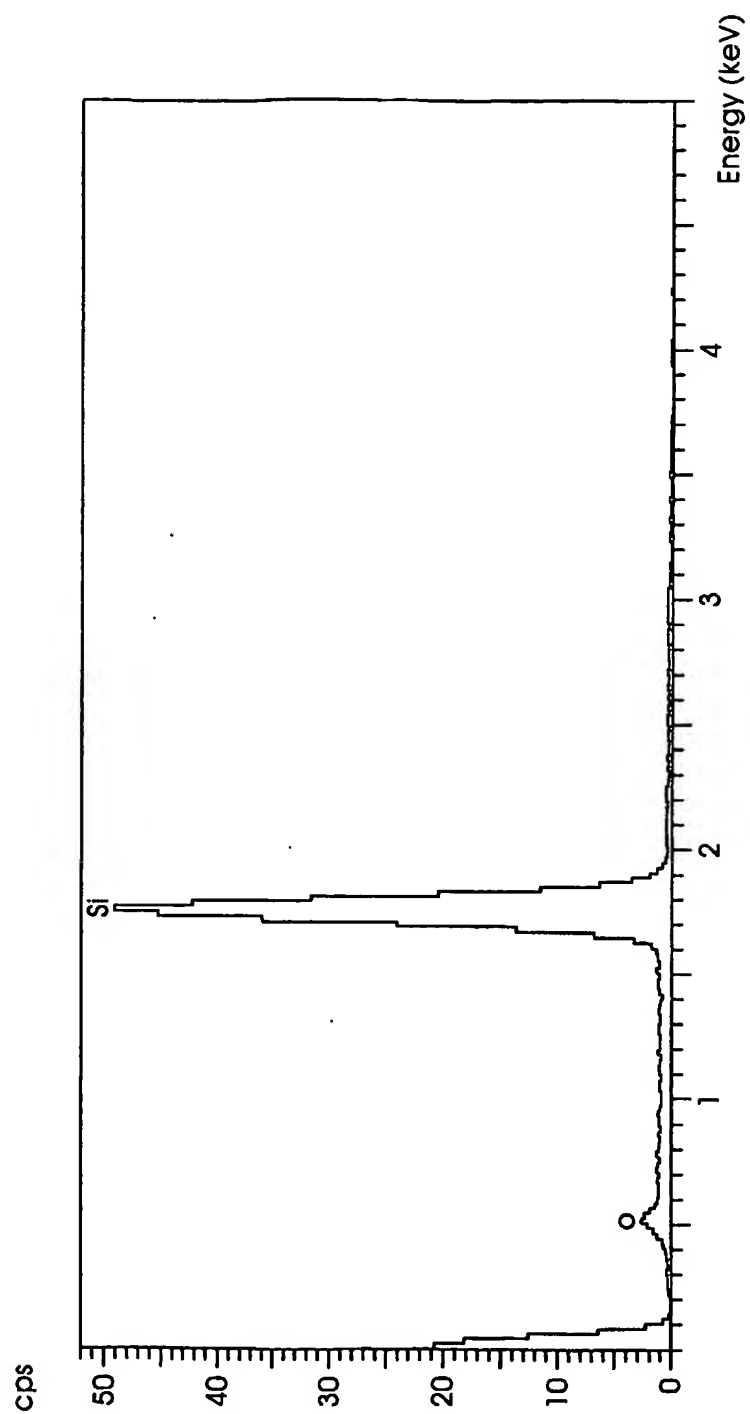


Fig. 9c

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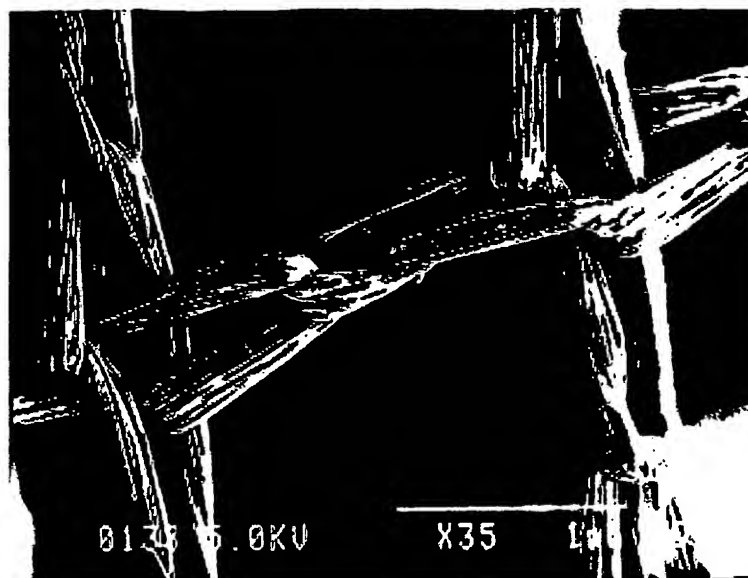


Fig. 10a



Fig. 10b

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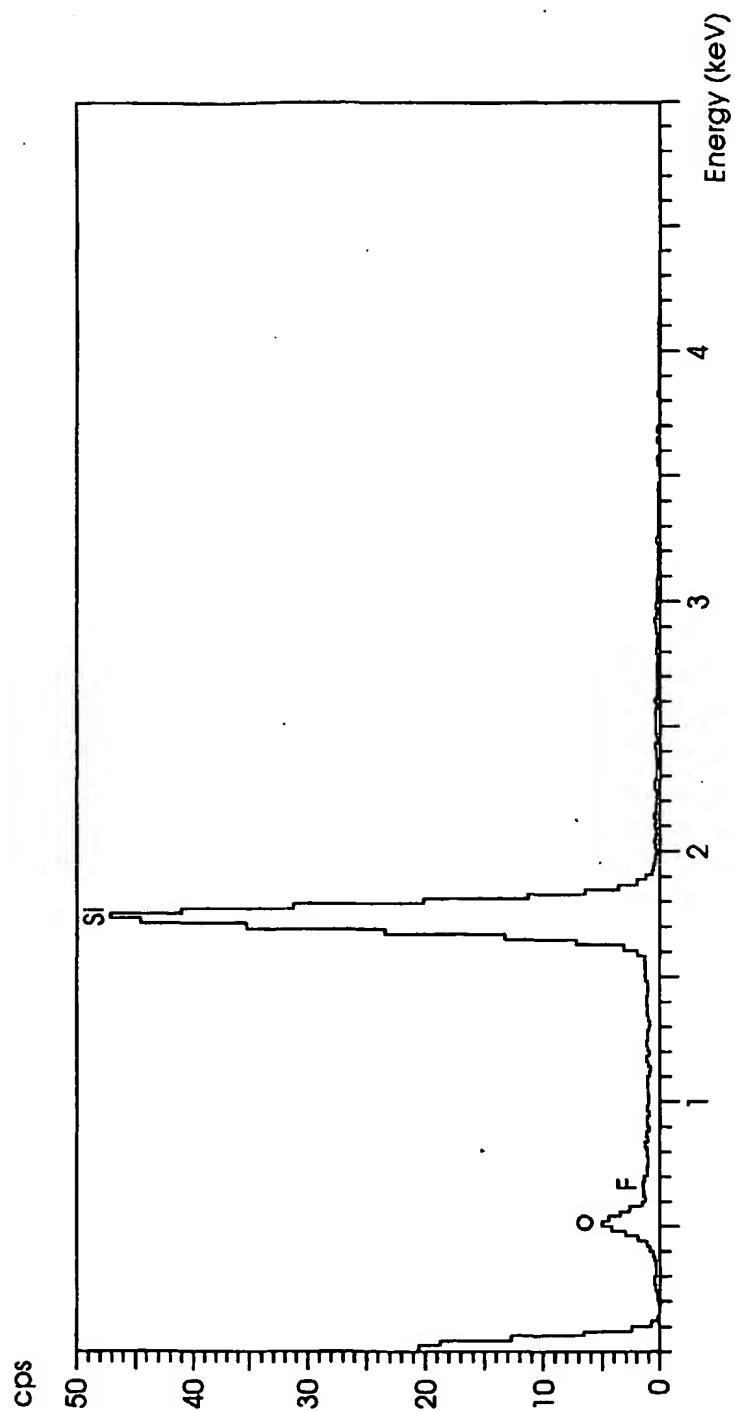


Fig. 10c

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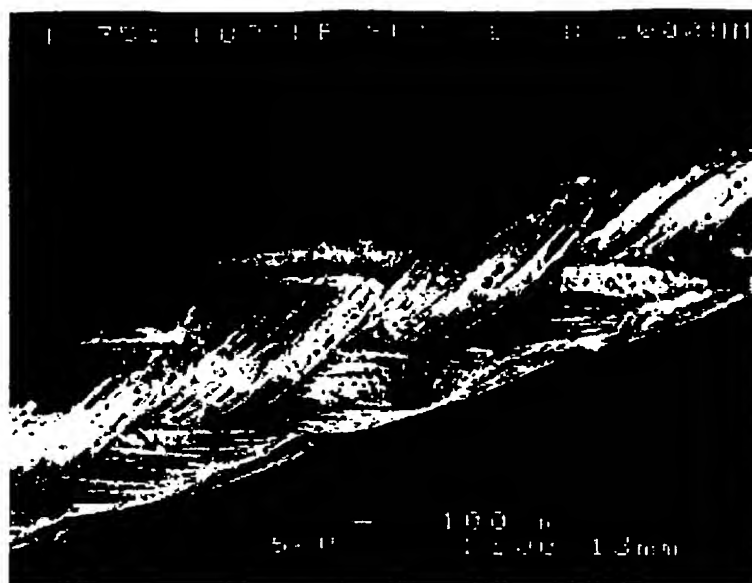


Fig. 11a

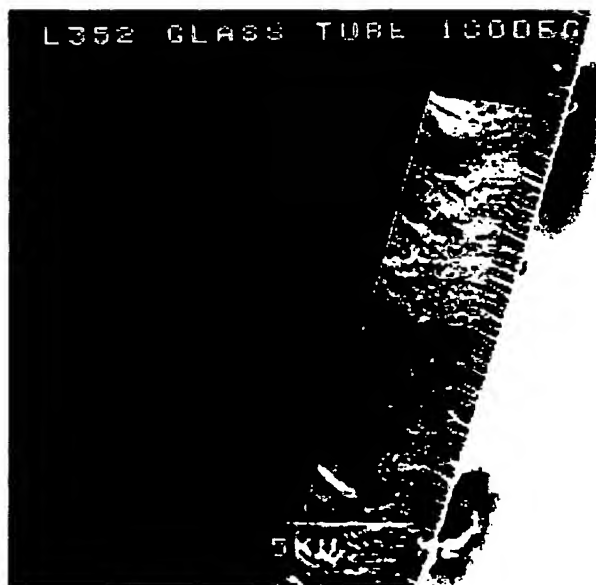


Fig. 11c

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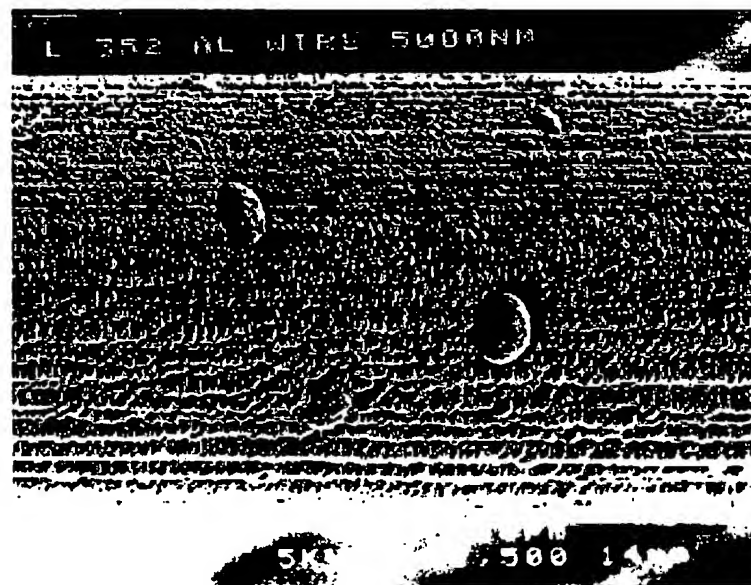
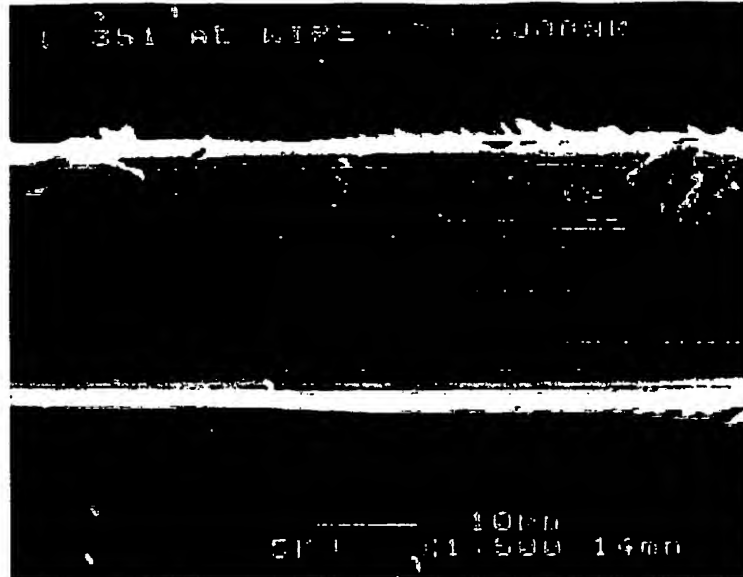


Fig. 11b

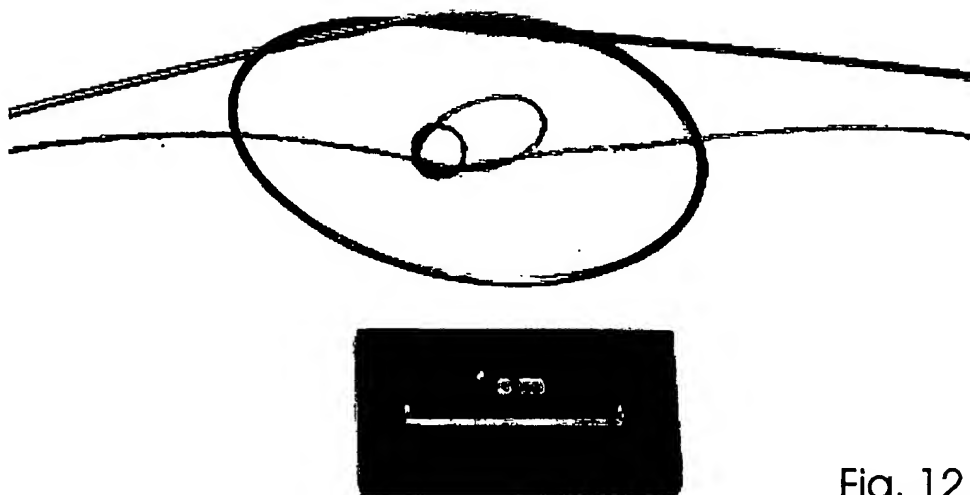


Fig. 12

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/05853

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61L15/08 A61L27/04 D01F9/08 A61B10/00 A61F7/00  
 D06M11/77 A61L17/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61L D01F A61B D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal, INSPEC, COMPENDEX, BIOSIS, EMBASE, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 363 115 A (QINETIQ LTD ;SECR DEFENCE (GB)) 12 December 2001 (2001-12-12) abstract	1
A	<p>---</p> <p>CANHAM L ET AL: "Will a chip every day keep the doctor away? S1 implants" PHYSICS WORLD, JULY 2001, IOP PUBLISHING, UK, vol. 14, no. 7, pages 27-32, XP008010482 ISSN: 0953-8585 the whole document</p> <p>---</p> <p>---/--</p>	1

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&amp;\* document member of the same patent family

Date of the actual completion of the international search

15 April 2003

Date of mailing of the international search report

06/05/2003

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Muñoz, M

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/GB 02/05853

## Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
**see FURTHER INFORMATION sheet PCT/ISA/210**
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.



## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

## Continuation of Box I.2

In view of the large number and also the wording of the claims (28 independent claims) presently on file, which render it difficult, if not impossible, to determine the matter for which protection is sought, the present application fails to comply with the clarity and conciseness requirements of Article 6 PCT (see also Rule 6.1(a) PCT) to such an extent that a meaningful search is impossible.

Moreover, the present claims relating to silicon containing fibres, threads, yarns or fabrics relate to an extremely large number of possible products as their subject-matter encompasses any silicon containing compounds whether it be or organometallic or mineral. Support within the meaning of Article 6 PCT and disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the products.

In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible.

Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the porous or mesoporous silicon containing fibres for use as medical fibres and medical fabrics as well as parts relating to products which can be obtained from those fibres and fabrics and their process of manufacture.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

## INTERNATIONAL SEARCH REPORT

Int'l Application No  
PCT/GB 02/05853

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	HETKE J F ET AL: "Silicon ribbon cables for chronically implantable microelectrode arrays" IEEE TRANSACTIONS ON BIOMEDICAL ENGINEERING, APRIL 1994, USA, vol. 41, no. 4, pages 314-321, XP002238344 ISSN: 0018-9294 cited in the application abstract ---	1
A	US 5 336 360 A (NORDINE PAUL C) 9 August 1994 (1994-08-09) claims 1,6 example 3 ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 03, 27 February 1998 (1998-02-27) & JP 09 296366 A (TAKAMATSU KUNIAKI; OHARA TOYOKO; KIKUCHI HIDEAKI; ITO YOSHIKI), 18 November 1997 (1997-11-18) abstract ---	1
A	US 5 053 248 A (HAKAMATA SHIGEYA ET AL) 1 October 1991 (1991-10-01) examples 1-4 claims 1,5 ---	1
P, X	WO 02 067998 A (CANHAM LEIGH TREVOR ; ASTON ROGER (GB); PSIMEDICA LTD (GB)) 6 September 2002 (2002-09-06) page 3, line 10 - line 30 -----	1

## INTERNATIONAL SEARCH REPORT

Inventor's International Application No

PCT/GB 02/05853

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 2363115	A	12-12-2001	AU 7421701 A EP 1296725 A1 WO 0195952 A1	24-12-2001 02-04-2003 20-12-2001
US 5336360	A	09-08-1994	US 5126200 A US 5549971 A US 5399430 A AU 610519 B2 AU 7853987 A BR 8707778 A CA 1283262 A1 EP 0318506 A1 IL 83528 A JP 2500758 T WO 8801204 A1	30-06-1992 27-08-1996 21-03-1995 23-05-1991 08-03-1988 31-10-1989 23-04-1991 07-06-1989 18-07-1991 15-03-1990 25-02-1988
JP 09296366	A	18-11-1997	JP 2972783 B2	08-11-1999
US 5053248	A	01-10-1991	NONE	
WO 02067998	A	06-09-2002	WO 02067998 A2	06-09-2002

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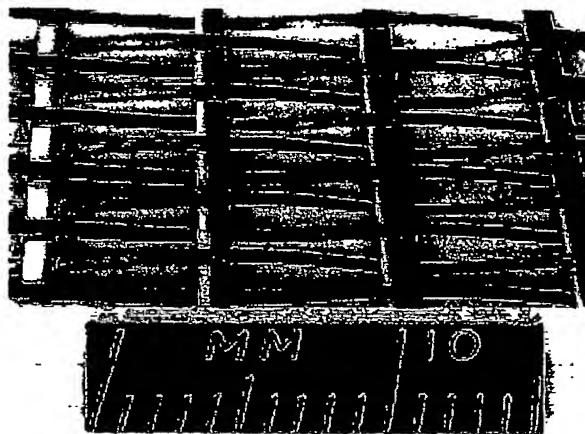
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MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE,  
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VC, VN, YU, ZA, ZM, ZW.

[Continued on next page]

(54) Title: MEDICAL FIBRES & FABRICS



(57) Abstract: A fibre or fabric comprising silicon for use as a medical fibre or fabric. The silicon present can be biocompatible, bioactive or resorbable material and may also be able to act as an electrical conductor. In addition, porous silicon may be used as a slow release means for example for drugs or fragrances, or as a collector for example for sweat. Novel fibres, fabrics and methods of preparation of these are also described and claimed.

WO 03/055534 A1



(84) **Designated States (regional):** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— with international search report

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2 October 2003

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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

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